Diesel Exhaust Particle Morphology

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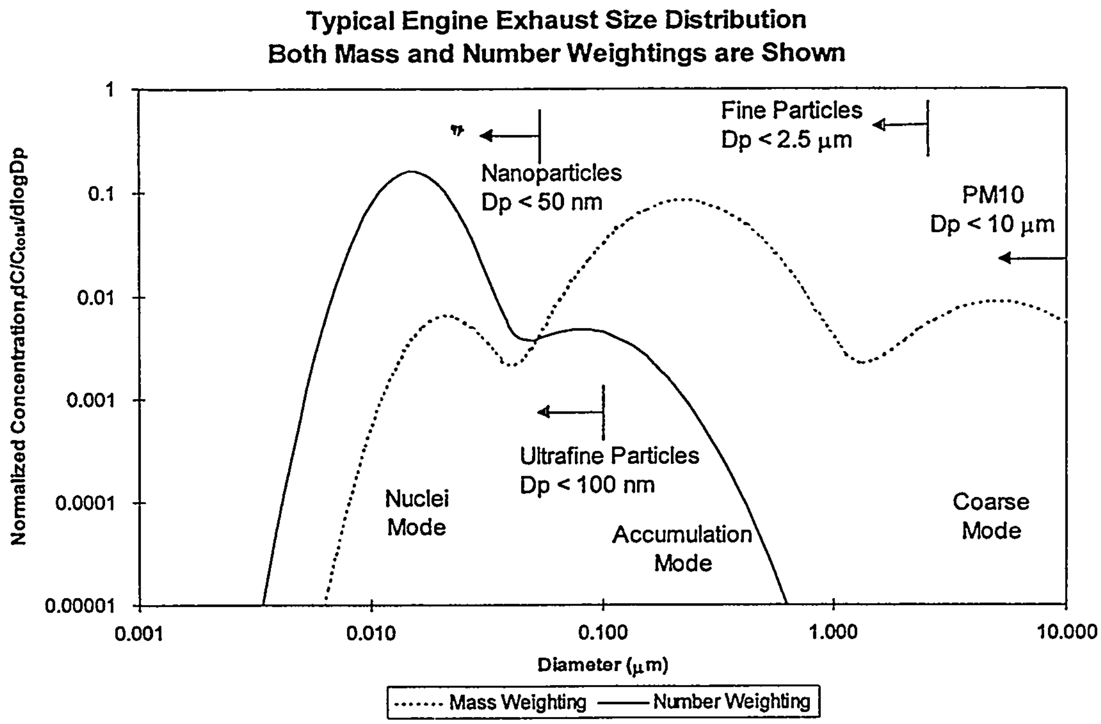
Background

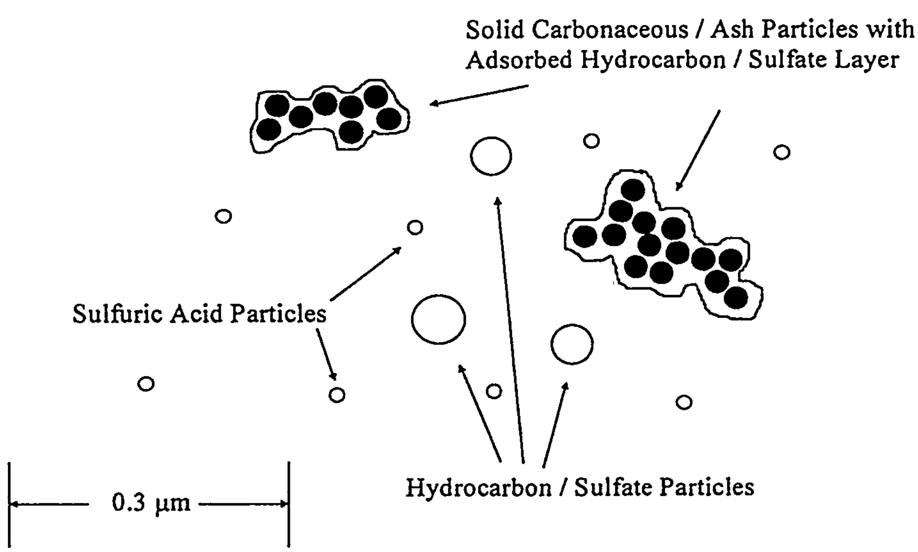
- Current emission standards are mass based. Recently interest in other measures, i.e, size, number, surface, has increased.
- Concerns about particle size
  - New ambient standards on fine particles
    - Correlations between fine particles and excess deaths
    - Increased asthma in children living near roadways
    - Special concerns about ultrafine and nanoparticles
  - Indications that reductions in mass emissions may increase number emissions
    - HEI study on old and new technology engines
    - High number concentrations downstream of some exhaust filters
    - Removing carbon from exhaust may make formation of tiny particles from fuel and lube oil derivatives more likely
  - Difficulties associated with measurement of ultrafine and nanoparticles
    - Often more than 90% of particle number are formed during exhaust dilution
    - Particle dynamics during sampling and dilution are highly nonlinear - large changes in of particle number may result from small changes dilution and sampling conditions

Typical Diesel Particle Size Distribution - Log Scale

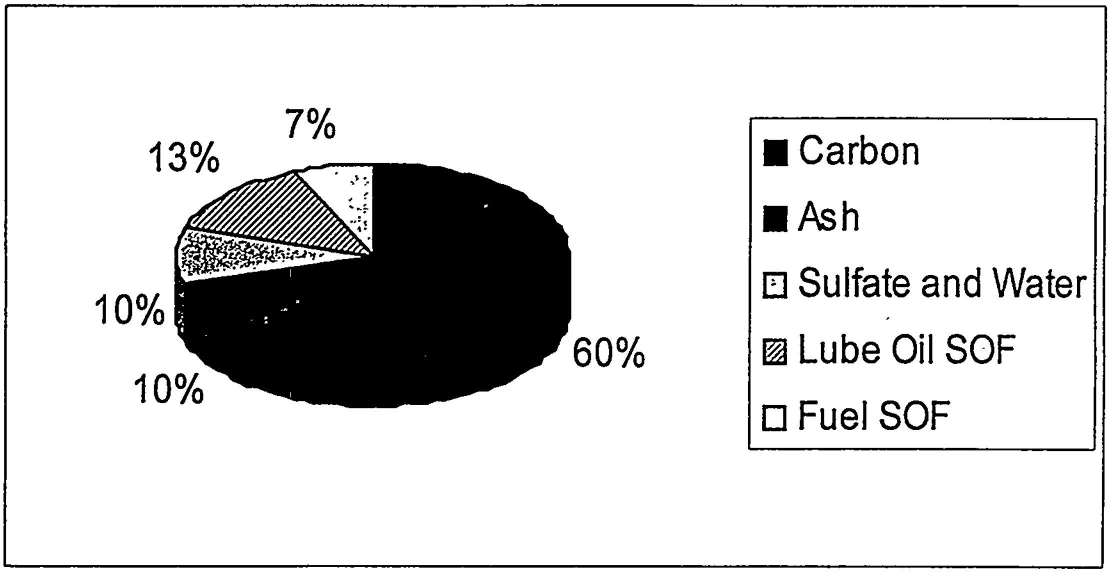


Particle Composition and Structure

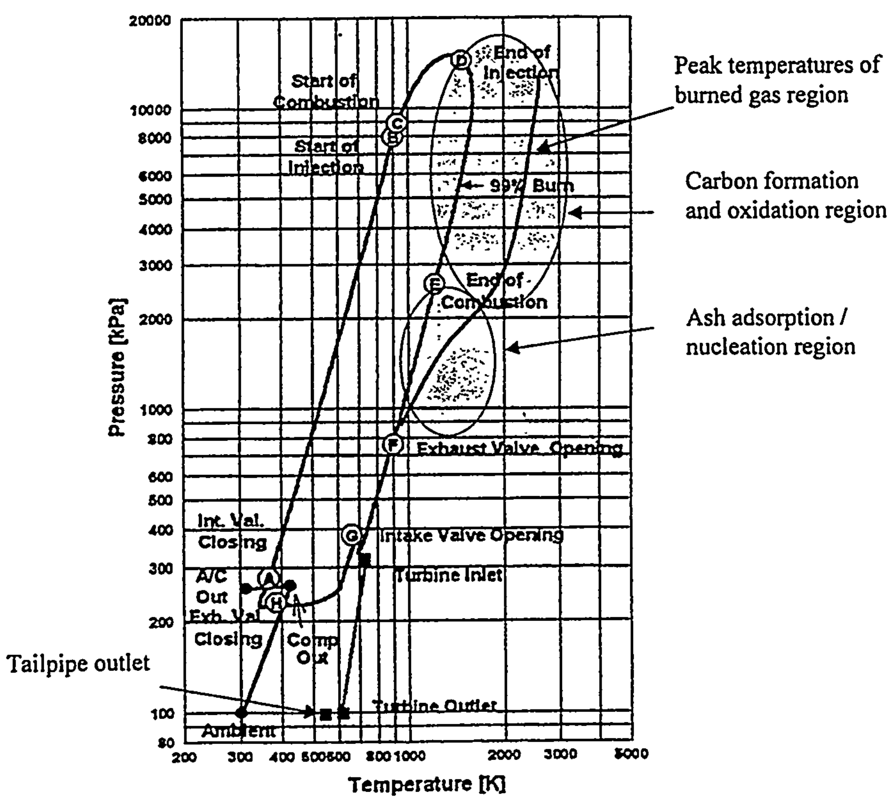
Particles consist mainly of highly agglomerated solid carbonaceous material and ash and volatile organic and sulfur compounds.



Typical Composition of Diesel Particulate Matter: Lube oil contributes to SOF, ash, sulfate

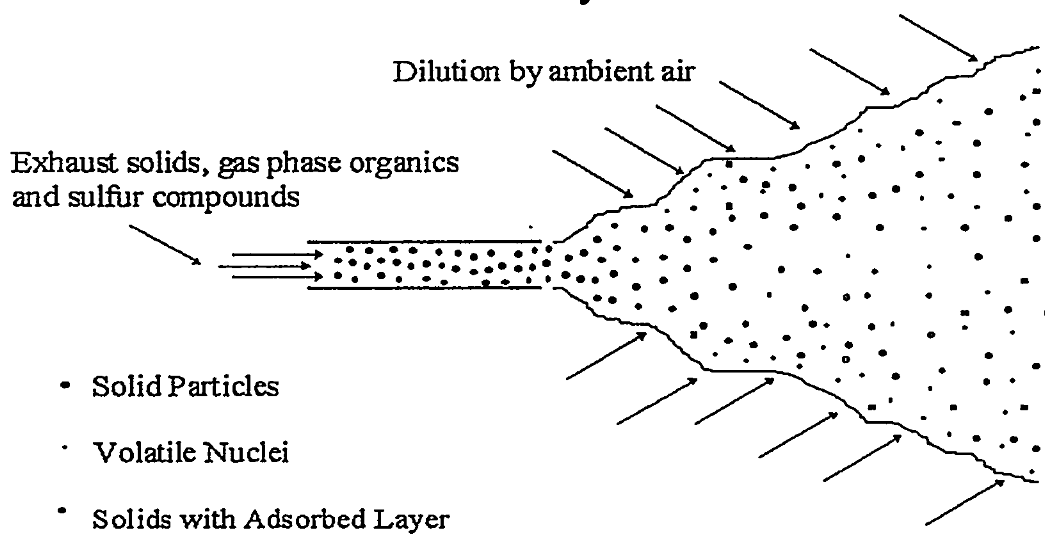


Typical P - T (average) plot for modern Diesel (adapted from Cummins, SAE 1999-01-0516)

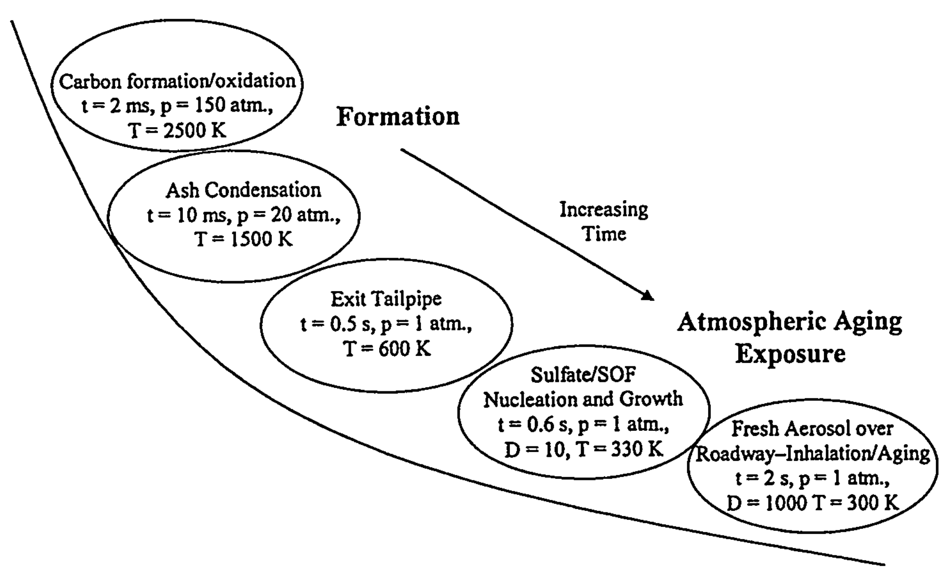


Atmospheric Dilution Leads to Nucleation, Absorption, and Adsorption

A dilution ratio of 1000 may be reached in 1 - 2 s



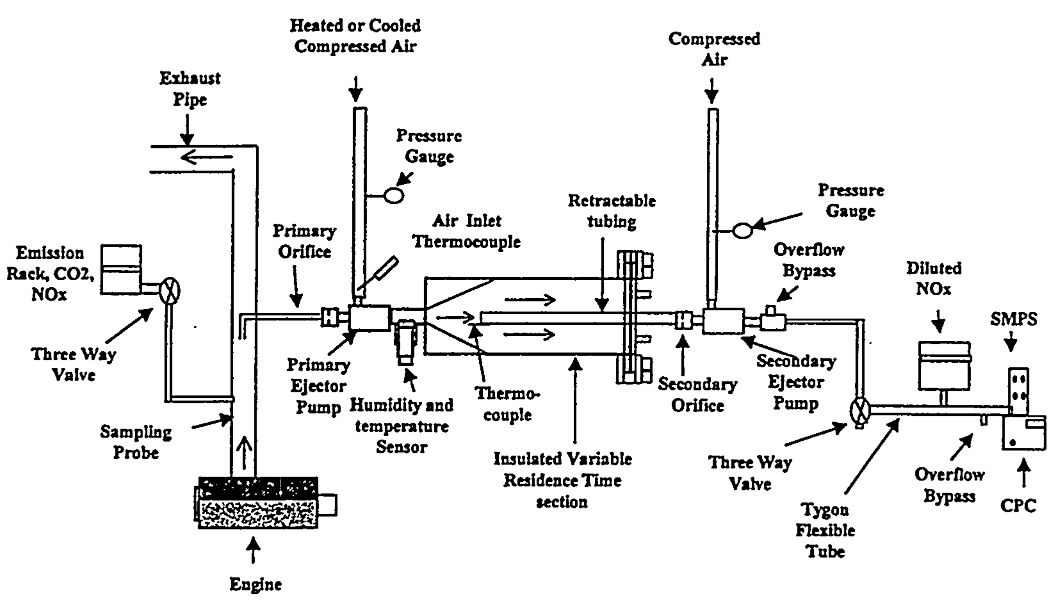
Particle Formation History: From the Start of Combustion to the Nose



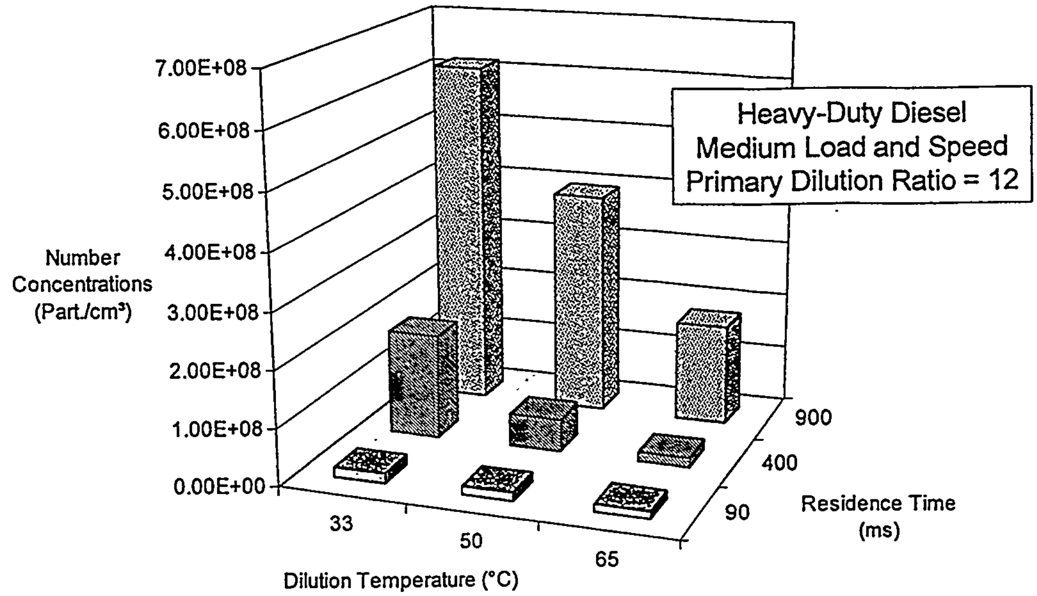
Significant Gas to Particle Conversion Takes Place as the Exhaust Dilutes and Cools

- More than 90% of the particle number may form through homogeneous nucleation of nanoparticles
- From 5 to more than 50% of the particle mass may form through adsorption, absorption, and nucleation
- These processes are *extremely* sensitive to dilution conditions
- Thermodynamics and fluid mechanics of mixing during dilution are very complicated and vary widely

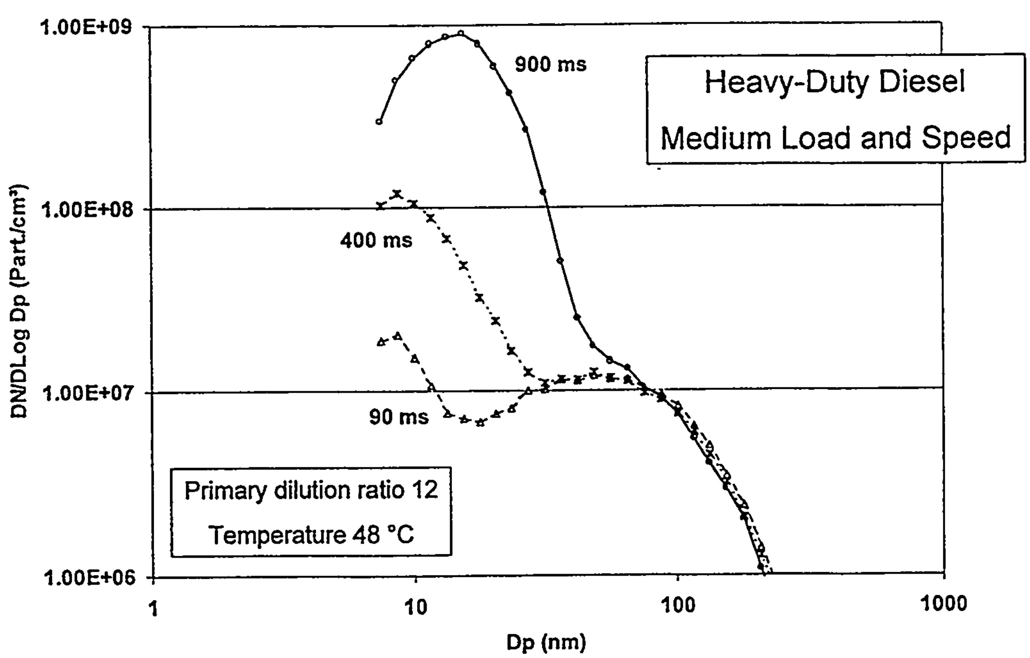
Studies of Diesel Nanoparticle Formation Using a Variable Residence Time Dilution System



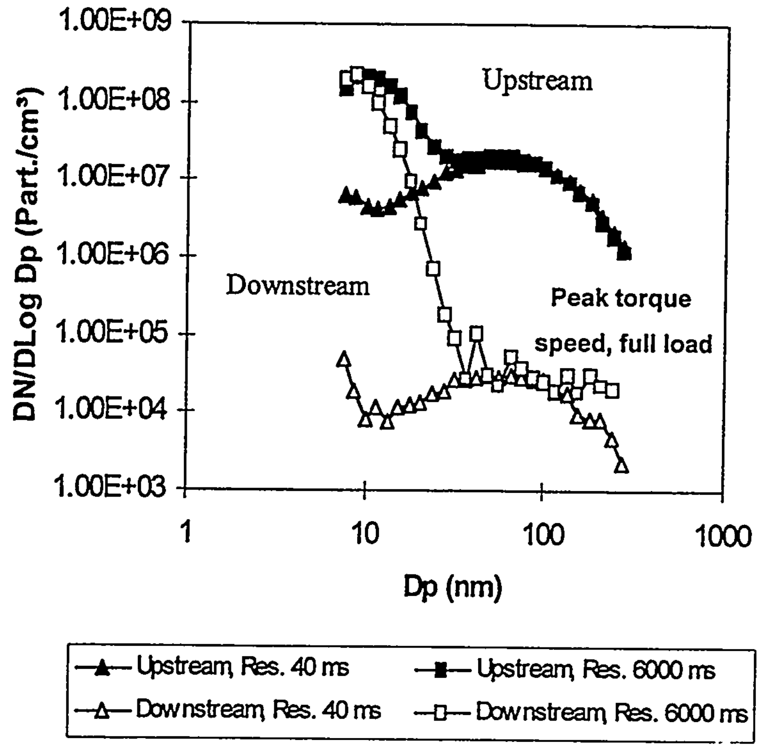
Sensitivity of Diesel Particle Number Emissions to Dilution Conditions - Residence Time and Temperature Effects



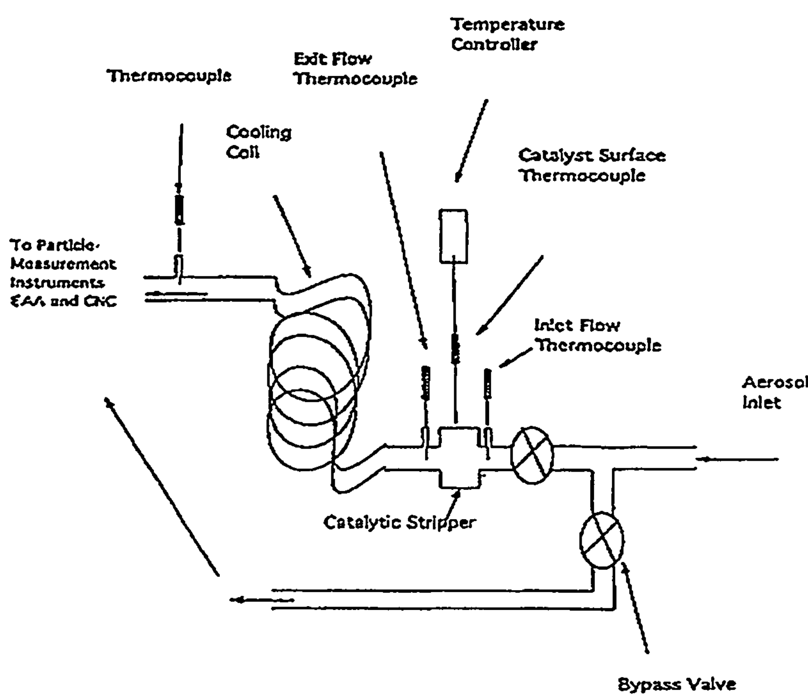
Sensitivity of Diesel Particle Size Distribution to Dilution Conditions - Residence Time Effects



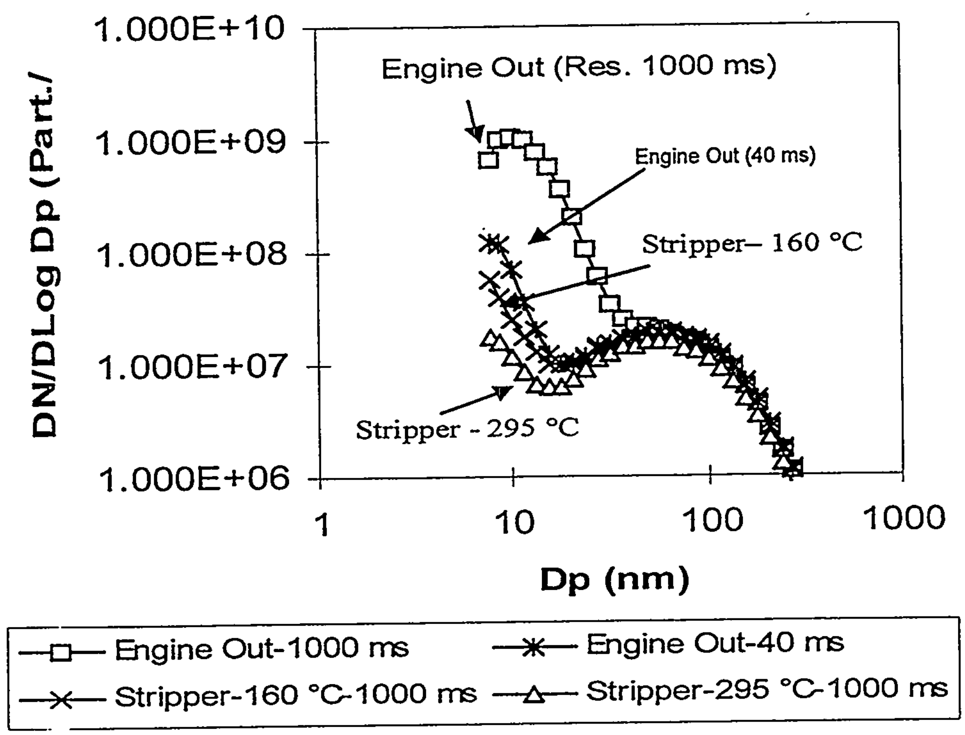
Nanoparticle formation downstream of an exhaust filter may be even more sensitive to dilution conditions



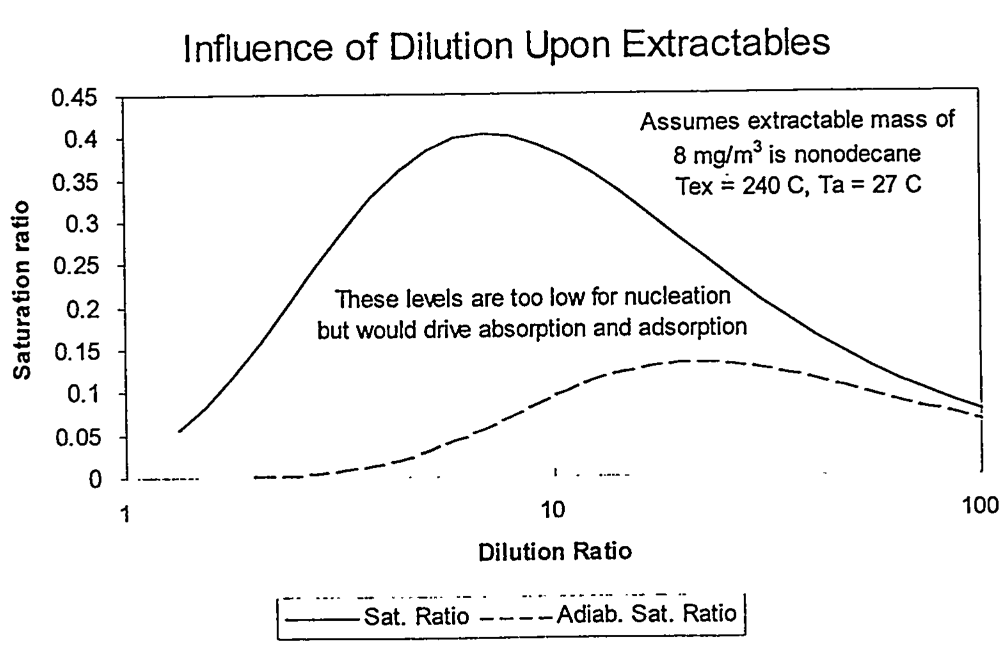
Our results suggest nanoparticles are mainly volatile, we have demonstrated this with a catalytic stripper



Typically more than 99% of the nanoparticles disappear by 300 C, the residue is likely to be metallic ash



For typical diesel exhaust conditions, saturation ratio may not be high enough for nucleation, S > ~ 3



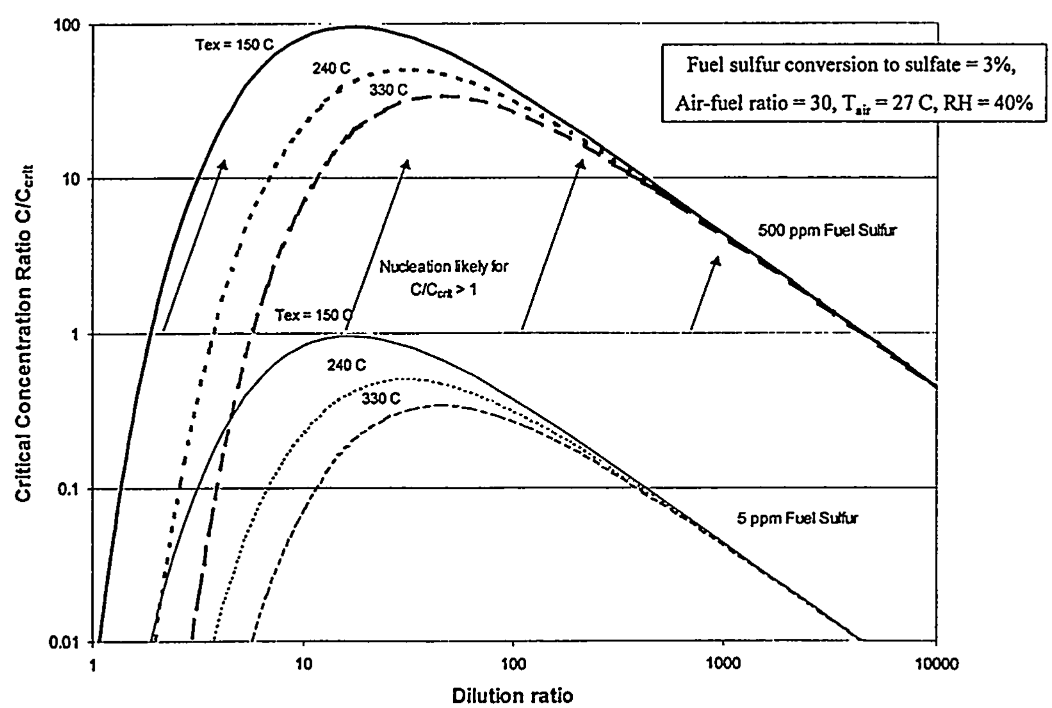
What does nucleate? Consider the threshold for Binary H_2SO_4-H_2O nucleation

- An extreme dependence of the nucleation rate upon temperature, H_2SO_4, and H_2O concentrations makes theoretical predictions of nucleation difficult.
- Seinfeld and Pandis give an empirical expression to predict the onset of nucleation in this system:

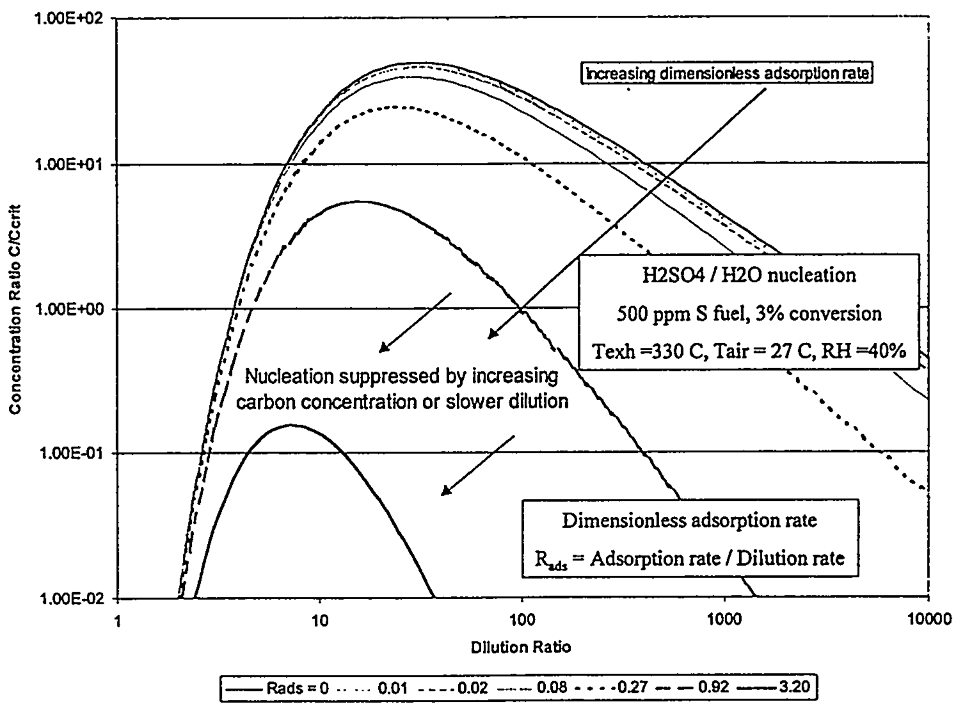
$$C_{crit} = 0.16\exp(0.1T - 3.5RH - 27.7)$$

  where C_{crit} is the threshold H_2SO_4 concentration in $\mu g/m^3$, T is temperature, RH is relative humidity (0 to 1).
- I have used this expression and mass and energy balances applied to the dilution process to predict the ratio of the actual H_2SO_4 concentration to the critical one, C/C_{crit}. When this critical concentration ratio exceeds one, nucleation is likely.

Influence of Fuel and Exhaust Conditions on Sulfuric Acid Nucleation



H_2SO_4 Nucleation Is Suppressed by Adsorption on Carbon Particles



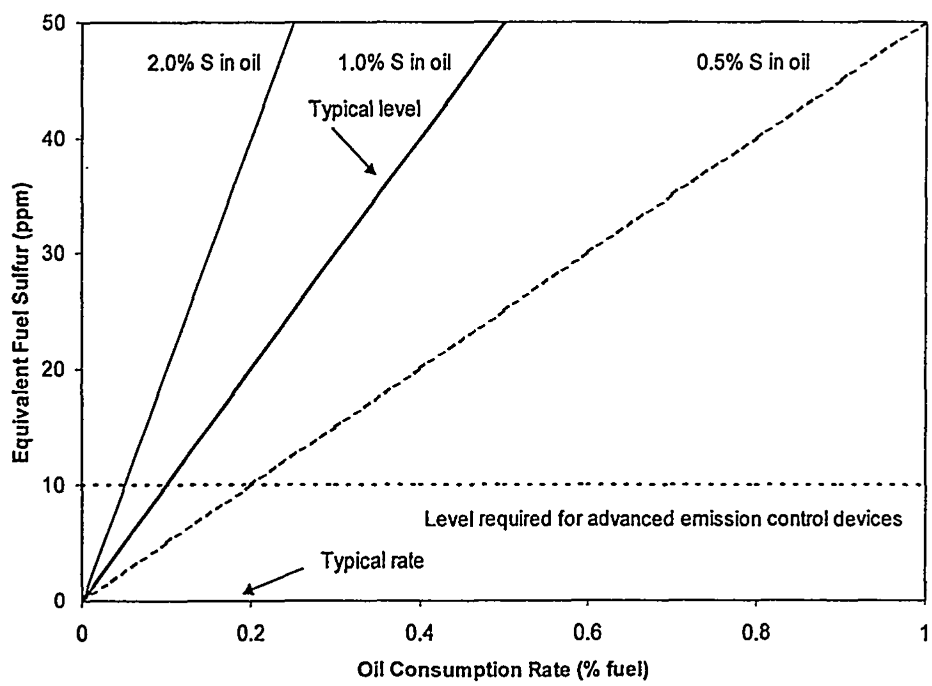
Nanoparticle Nucleation and Growth

- It appears that with current engines binary sulfuric acid - water nucleation triggers the process.
- The initial size of these nuclei is about 1 nm.
- In most cases there is not enough sulfuric acid present in the exhaust to explain the observed rates of particle growth.
- Hydrocarbons normally associated with the soluble organic fraction apparently are absorbed by the concentrated sulfuric acid nuclei leading to the observed growth rates.
- Solid carbon in the exhaust adsorbs particle precursors and suppresses both nucleation and and growth of nanoparticles
- Fast dilution decreases the influence of solid carbon and the time available for nucleation and growth

Lubricating oil and emissions

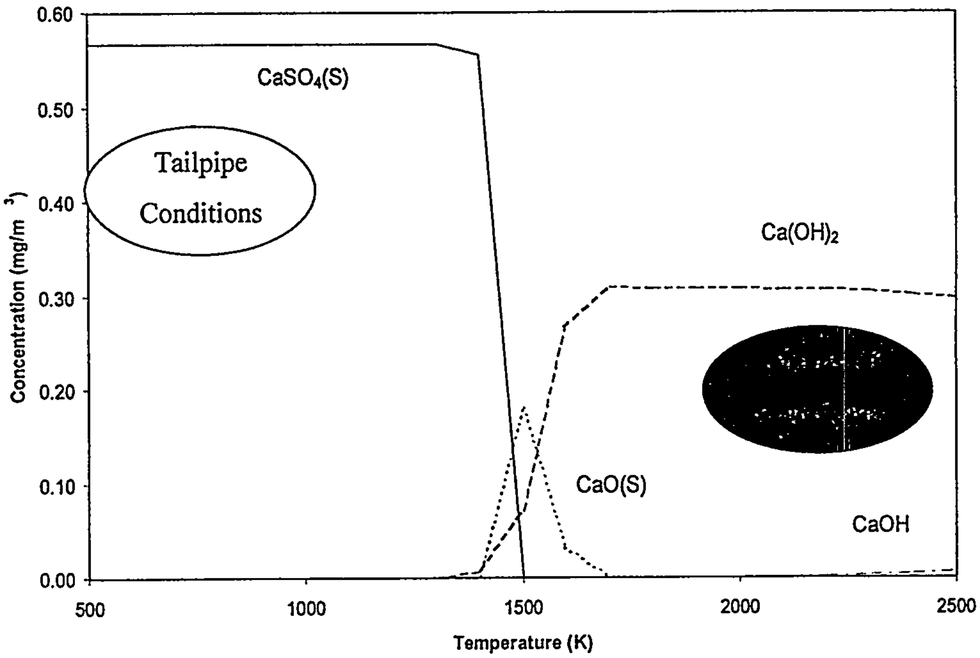
- Direct influences on particulate emissions
  - Sulfur in oil contributing to sulfuric acid in the exhaust
  - Lube oil contribution to SOF
    - Adsorbed SOF mass on solid carbon particles
    - High SOF leads to faster nanoparticle growth, especially with low solid carbon emitters
  - Ash particles
    - Most ash incorporated into accumulation mode on current engines
    - Direct ash nucleation to form nanoparticles may be an issue with low solid carbon emission engines
- Other Influences on Emissions
  - Sulfur and phosphorus damage to aftertreatment devices
  - Crankcase fumes and positive crankcase ventilation

The lube oil may contribute more sulfur to the exhaust than the fuel with future ultra-low sulfur fuels



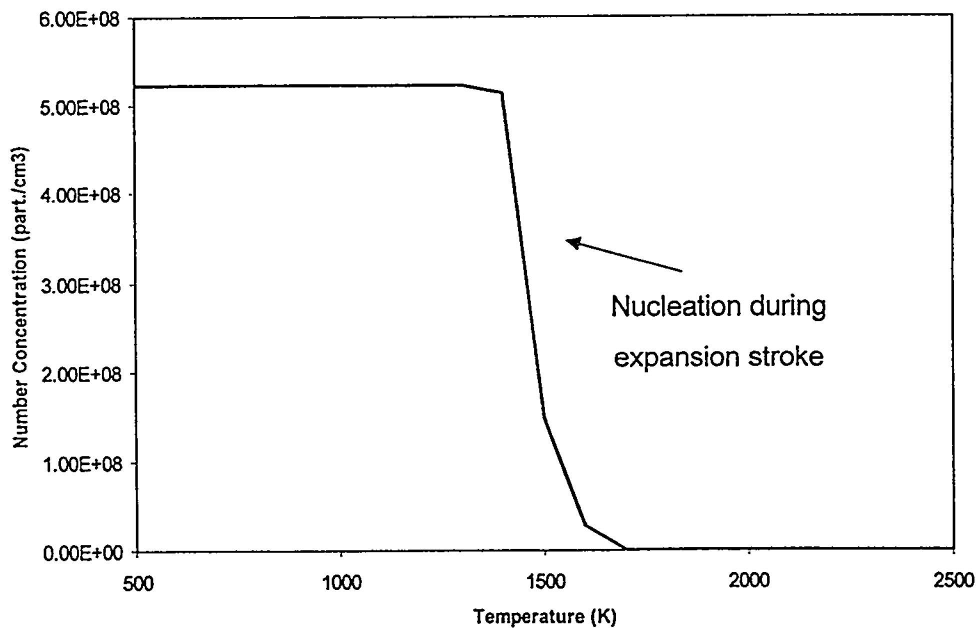
Calcium from the oil will form exhaust solids as the products of combustion cool during expansion stroke

Modern Engines Have Particle Mass Concentrations in the Range of 8 mg/m^3



If there is little carbon formed by combustion, ash particles may nucleate to form solid nanoparticles

Number Concentrations of Calcium Particles -
Assumes all of the calcium compounds nucleate to form 7 nm diameter nanoparticles.



Summary - 1

- A significant amount of particulate matter (e.g. 90 % of the number and 30% of the mass) is formed during exhaust dilution from material present in the vapor phase in the tailpipe, principally sulfuric acid from sulfur in the fuel and lube oil and SOF constituents from the fuel and lube oil.
  - New particles are formed by nucleation. This is likely to be the source of most of the ultrafine and nanoparticles (and particle number) associated with engine exhaust.
  - Preexisting particles grow by adsorption or condensation.
  - Nucleation and adsorption are competing processes. Soot agglomerates provide a large surface area for adsorption that suppresses nucleation. Thus, engines with low soot mass emissions may have high number emissions.

Summary - 2

- Nanoparticle measurements are very strongly influenced by the sampling and dilution techniques employed.
  - Nucleation, adsorption, absorption, and coagulation during sampling and dilution depend upon many variables, including dilution rate, (or residence time at intermediate dilution ratio), humidity, temperature, and relative concentrations of carbon and volatile matter.
  - Changes of more than two orders of magnitude in nanoparticle concentration may occur as dilution conditions are varied over the range that might be expected for normal ambient dilution, e.g., 0.1 to 2 s dilution time scales.
- Sampling systems should mimic atmospheric dilution to obtain samples representative of the tailpipe to nose process.

The most difficult problem associated with exhaust particle measurement is understanding the dilution process from tailpipe to nose -- this is being examined in the CRC E-43 program

Summary - 3

- Currently most nanoparticles are volatile. However, with cleaner engines, metallic ash particles from the lube oil (or fuel if metallic additives are present) may become more important.
  - Solid particles raise new issues...
  - But they are easy to control with exhaust filters
- Spark ignition engines have much lower fine PM mass emission rates than diesels but their greater numbers may make them an important fine PM source.
  - SI particles are considerably smaller than those from diesel engines so that they will be a much larger relative contributor to nanoparticle emissions than to mass emissions
  - Lube oil also plays an important role in SI PM emissions
    - Much of the mass is lube oil related SOF in older high emitters
    - With clean low emitters, lube oil ash may be the principal PM constituent (Leeds University)